1990

Inequivalent models of irreversible dimer filling: "Transition state" dependence

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Abstract
Irreversible adsorption of diatomics on crystalline surfaces is sometimes modeled as random dimer filling of adjacent pairs of sites on a lattice. We note that this process can be implemented in two distinct ways: (i) randomly pick adjacent pairs of sites, *jj'*, and fill *jj'* only if both are empty (horizontal transition state); or (ii) randomly pick a single site, *j*, and if *j* and at least one neighbor are empty, then fill *j* and a randomly chosen empty neighbor (vertical transition state). Here it is instructive to consider processes which also include competitive random monomer filling of single sites. We find that although saturation (partial) coverages differ little between the models for pure dimer filling, there is a significant difference for comparable monomer and dimer filling rates. We present exact results for saturation coverage behavior for a linear lattice, and estimates for a square lattice. Ramifications for simple models of CO oxidation on surfaces are indicated.

Disciplines
Biological and Chemical Physics | Physics

Comments
This article is published as Nord, R. S., and J. W. Evans. "Inequivalent models of irreversible dimer filling:"Transition state"dependence." *The Journal of chemical physics* 93, no. 11 (1990): 8397-8398, doi:10.1063/1.459273. Posted with permission.

Inequivalent models of irreversible dimer filling: "Transition state" dependence

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(Received 24 July 1990; accepted 24 August 1990)

Irreversible dimer filling has long been used as a model for immoble adsorption of diatomics onto adjacent pairs of adsorption sites.[1-4] Of particular interest is the nonequilibrium saturation state which contains a distribution of unfillable isolated empty sites. Dimer filling is also of interest as a key component of simple models for CO oxidation.[5] (O_2 adsorption is modeled as dimer filling, and CO adsorption as competitive monomer filling of single sites.)

However, it is rarely noted that dimer filling can be implemented in one of two natural but inequivalent ways.[4,6,7] Model (i): randomly pick adjacent pairs of sites, jj', and fill jj' only if both sites are empty. Note that one can either pick the pair of sites simultaneously, or first pick one site, j, and (if empty) then randomly choose a neighbor, j' (filling only if both are empty). Model (ii): randomly pick single sites, j, and if j and at least one neighbor are empty, then fill j and a randomly chosen *empty* neighbor, j' (see Fig. 1). The distinction between the models derives from the difference between randomly choosing j' from among all neighbors or from among only empty neighbors.

It seems appropriate to associate the "standard dimer filling" model (i) with adsorption of diatomics having horizontal transition states (parallel to the surface). On the other hand, for vertical transition states, one anticipates that once the lower atom is in place over an empty site, the top atom will rotate toward an empty neighboring site (should one exist), in order to adsorb. This corresponds to the "end-on dimer filling" model (ii).

Here we analyze models involving competition between irreversible random monomer and dimer filling with attempt rates y_m and y_d, respectively. Thus for short times, t, the monomer and dimer partial coverages behave like $\theta_m \sim y_m t$ and $\theta_d \sim 2y_d t$, respectively. Without loss of generality, we set $y_m + y_d = 1$. For a linear (or Bethe) lattice, exact analysis is possible by virtue of a shielding property of single empty sites for model (i), and empty pairs for model (ii).[8] Here we present closed form expressions for saturation partial coverages as functions of y_m or y_d. We note that a cooperative version of model (i) has been considered previously,[9] and the most general exactly solvable version of the model has also been described.[10] The shielding property extends to higher dimensions, but does not allow exact solution. For model (i) on a square lattice, we have previously implemented an approximate truncation of the exact hierarchical form of the master equations guided by the shielding property.[4] The same approach is here applied to model (ii). We also compare results from Monte Carlo simulations for models (i) and (ii) on a square lattice.

For a *linear lattice*, let P_n denote the probability of finding a string of n empty sites. Rate equations for the P_n follow from consideration of all possible ways such empty configurations can be destroyed by adsorbing monomers or dimers. All contributing terms are readily written in terms of the P_m (probability conservation rules are sometimes needed). One thus obtains, for model (i),

$$\frac{d}{dt}P_n = -ny_mP_n - (n-1)y_dP_n - 2y_dP_{n+1} \quad \text{for } n \geqslant 1. \tag{1}$$

The first term is associated with monomers filling, and the middle (last) terms with dimers filling completely overlapping (partly overlapping the ends of) the empty string. Equation (1) can be solved by noting that $P_{n+1}/P_n = e^{-t}$, for $n \geqslant 1$. For model (ii), one instead finds that

$$\frac{d}{dt}P_1 = -y_mP_1 - y_d(4P_2 - 2P_3),$$

$$\frac{d}{dt}P_n = -ny_mP_n - y_d(nP_n + 2P_{n+1} - P_{n+2}) \quad \text{for } n \geqslant 2, \tag{2}$$

which can be solved noting that $P_{n+1}/P_n = e^{-t}$, for $n \geqslant 2$. Partial coverages for monomers, θ_m, and dimers, θ_d, are most easily obtained from integrating the equation $d/dt\,\theta_m = y_mP_1$ and using $\theta_m + \theta_d + P_1 = 1$. Analysis of these equations to determine the saturation partial coverage of dimers, θ_d^{sat}, yields

$$\theta_d^{\text{sat}} = 2y_d \int_0^1 dx\, x^{y_m} e^{2y_d(x-1)} \quad \text{for model (i)},$$

$$\theta_d^{\text{sat}} = 2 - 2e^{y_d/2} \int_1^2 dx\, e^{-y_dx^2/2} \quad \text{for model (ii)}.$$

Of course $\theta_m^{\text{sat}} + \theta_d^{\text{sat}} = 1$, and θ_d^{sat} for model (ii) can be trivially reexpressed in terms of the error function, Erf.

For pure dimer filling ($y_d = 1$), one obtains

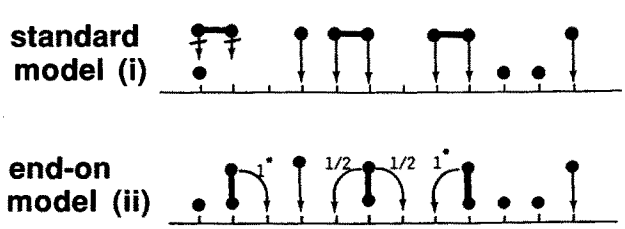

FIG. 1. Comparative schematic of competitive monomer and dimer filling using the standard model (i) (top) and the end-on model (ii) (bottom). The numbers on the bottom figure indicate the probabilities for various rotations. The standard model is recovered replacing 1* by 1/2.

 0021-9606/90/238397-02$03.00

TABLE I. Saturation dimer coverages for competitive random monomer and dimer filling on a linear lattice. Exact results for the standard and end-on models (i) and (ii), respectively, are compared.

$y_m:y_d$	0:1	1:3	1:2	1:1	2:1	3:1
Standard	0.864 66	0.668 77	0.601 27	0.461 92	0.315 86	0.240 02
End-on	0.876 68	0.723 07	0.664 33	0.533 42	0.381 85	0.297 11

$\theta_d^{\text{sat}} = 1 - e^{-2} \approx 0.864\ 66$ for model (i) recovering Flory's famous result,[11] and

$$\theta_d^{\text{sat}} = 2 - (2\pi e)^{1/2}[\text{Erf}(2^{1/2}) - \text{Erf}(2^{-1/2})]$$
$$\approx 0.876\ 68 \text{ for model (ii)}.$$

This slight difference between the saturation dimer coverages for the two models is increased significantly if one introduces competitive random monomer filling with a comparable filling rate (see Table I). Clearly this is a consequence of the feature that the standard dimer filling mechanism of model (i) is less efficient (i.e., slower) than the end-on dimer filling mechanism of model (ii).

For a *square lattice*, sophisticated approximate truncation of the exact hierarchical rate equations (Ref. 4) produces the results shown in Table II(A). Comparison with corresponding Monte Carlo simulation results [Table II(B)] demonstrates the remarkable accuracy of the truncation procedure. One sees the same trends as for the linear lattice except that here, end-on dimer filling is even more efficient relative to the standard model, especially for comparable monomer and dimer filling rates.

In summary, we have shown that the statistical characteristics of processes involving dimer filling can be quite sensitive to the details of the filling model implemented (which in turn reflects dynamical "transition state" aspects of the process). The existence of inequivalent dimer filling models has not been generally appreciated previously, e.g., Ref. 2 apparently uses model (ii), but attempts to compare with previous model (i) simulations. There are obvious ramifications for the recent simple models of CO-oxidation reactions, where the standard dimer filling model has been applied.[5] Using instead the end-on filling model will significantly change (increase) the y_m values for various poisoning transitions.[12]

TABLE II. Saturation dimer coverages for competitive random monomer and dimer filling on a square lattice. (A) Third-order severe truncation (Ref. 4, Sec. III) results. (B) Monte-Carlo simulation results with uncertainty $\pm 0.000\ 10$.

$y_m:y_d$	0:1	1:3	1:2	1:1	2:1	3:1
(A)						
Standard	0.906 34	0.668 46	0.596 52	0.454 65	0.310 68	0.236 56
End-on	0.921 04	0.767 28	0.708 86	0.578 18	0.423 68	0.334 70
(B)						
Standard	0.906 87	0.668 51	0.596 39	0.454 35	0.310 58	0.236 66
End-on	0.918 82	0.767 01	0.708 89	0.579 95	0.425 52	0.336 23

Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. J.W.E. was supported for this work by the Division of Chemical Sciences, Office of Basic Energy Sciences.

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